PREPARATION OF SALICYLIC ALDEHYDE

BY

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A. E. MAITRE

ARMOUR INSTITUTE OF TECHNOLOGY

1919

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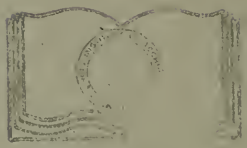

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The preparation of salicylic
aldehyde

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THE PREPARATION OF SALICYLIC ALDEHYDE

A THESIS

PRESENTED BY

C. B. CLARK AND A. E. MAITRE

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

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H. McCormack
Professor of Chemical Engineering

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Object

In our investigation of the synthesis of Coumarin we found salicylaldehyde to be the starting point in nearly every instance. As it was impossible to procure salicylaldehyde from any chemical supply house at a reasonable price we decided to investigate the synthesis of the aldehyde, and determine whether there was any process by which it could be obtained at a cost low enough to permit its use commercially. The literature on the subject was very limited and the only reliable references were of German origin. To the best of our knowledge the aldehyde is produced only in small quantities. What the demand for it would be, were it produced on a large scale at a reasonable price, we are unable to say, only trial could show that.

CHEMISTRY

Classification test of Aldehydes:

This definition admits to the group in addition to the true aldehydes those actals that are partially hydrolyzed to aldehydes under the conditions of the test, but excludes the aldose carbohydrates.

Test: Add 0.05 grm. of the finely powdered substance, if it is a solid, or one drop, if it is a liquid, to 5 c.c. of a Fuchsine Aldehyde Reagent and if the substance dissolves, allow the solution to stand two minutes and then observe the color. If the substance does not dissolve shake the test tube containing it gently for two minutes and then observe the color. Never apply heat.

The appearance of a distinct pink, red, purple, or blue coloration in the

solution within the time limit indicates that the compound tested is an aldehyde.

The Fuchsine Aldehyde Reagent;- Dissolve 0.2 grm. of rosaniline, or, if the free base cannot be obtained, of the hydrochloride or acetate, in 10 c.c. of a freshly prepared, cold, saturated aqueous solution of sulphur dioxide. Allow the solution to stand until all signs of pink disappear and it becomes colorless or pale yellow. This will require several hours. Then dilute with water to 200 c.c. and preserve for use in tightly stoppered bottles.

This reagent keeps well if not unnecessarily exposed to air and light. The directions for its preparation should be followed with care, since any large increase of sulphurous acid above the quantity specified diminishes its sensitiveness so

much as to render it unserviceable in testing for the less reactive aromatic aldehydes like salicylaldehyde, vanilline, etc. A reagent that has been in use many months and is found to have lost sensitiveness may be re-sensitized by the cautious addition of sodium acetate, stopping at the moment when a faint pink coloration begins to appear, and then discharging this color by the addition of a few drops of the oxidized solution held in reserve for this purpose. In this connection it should be stated by way of caution, that free alkali, or the alkali salt of any weak acid, organic or inorganic, will redden the reagent like in aldehyde. It is also reddened by heat or when exposed in small quantities to the air for some hours at the ordinary temperature. Mineral acids greatly di-

minish its sensitiveness.

Observations on Test:

Soluble aldehydes usually color the fuchsine reagent within a few seconds; those which are difficulty soluble and of high molecular weight sometimes require the full two minutes. Solid substances which for any reason are suspected to be polymerized aldehydes should be boiled with 5 c.c. of water containing a drop of strong hydrochloric acid, if no color appears within the time limit, and a few drops of the cooled solution then added to the reagent. Enough of the compound (e.g. metaaldehyde) may thus be depolymerized to give a good reaction.

Properties of Salicylic Aldehyde: ($O\text{-}HO.C_6H_4.CHO$) is a liquid with a pleasant aromatic smell and a luring spice-like taste; it boils at 196.5°, solidifies

at minus 20° to large crystals, and has a specific gravity of 1.1731 at 13.5°. Difficulty soluble in aqueous. Very soluble in alcohol and ether. Aqueous soluble gives with Fe Cl3 intense violet color. Convert into the phenylhydrazine.

General, Physical and Chemical Characteristics of the Aldehydes

Nearly all aldehydes of the liquid division are distinguished by characteristic odors, which, for the more volatile species, may be described as ethereal and at the same time imitating or pungent; and for the higher boiling ones, as aromatic, fragrant or spicy. The solid aldehydes are either odorless or have odors similar to those of the higher boiling liquid aldehydes, though as a rul less intense.

Aldehydes are notable chemicals for the reactivity of its species. Brief contact with small quantities of concentrated mineral acids, alkalies or certain metallic salts often causes gradual or sudden polymerization of aldehyde to more stable "para" or "meta" modifications, which would entirely fail to give aldehydic reactions were it not for their tendency to dissociate to some slight extent, under the influence of reagents, to the parent compound.

The liquid aldehydes are gradually oxidized to acids by exposure to the air, and commercial preparations will often be found to react acid towards litmus or phenolphtholein. Aldehydes are readily oxidized by alkaline permanganate and by ammoniacal silver nitrate. The latter reaction which is accompanied by

the formation of a silver mirror, or a precipitate of finely divided metallic silver, is a simple and valuable test.

Aldehydes usually dissolve in concentrated sulphuric acid with decomposition. Hot solutions of caustic alkali attack them with greater or less ease, according to the species, forming salts of organic acids and afe sometimes accompanied by other products. Bromine reacts with them readily, hydrobromic acid being evolved. Metallic sodium attacks them much as it does alcohols or phenols, hydrogen being sometimes liberated. Phenylhydrazine, hydroxylamine and aniline condense with them to hydrazones oximes, and anils, compounds which often crystallize well, and are very valuable in the identification of individual species. Phenylhydrazine,

applied in the proper manner, is also a very sensitive general reagent for detection of the carbonyl radical in aldehydes.

Towards certain reagents like sodium bisulphite, many aldehydes, as well as ketones, act like unsaturated compounds. A concentrated bisulphite solution, when vigorously shaken in a test tube with an equal volume of a liquid aldehyde, or with a concentrated ethereal solution of the solid aldehyde, frequently evolves heat and solidifies, either at once, or after being cooled and shaken, to a thick crystalline magma of the composition, R. C. H (OH) (SO_3Na), from which the original aldehyde may be recovered by treatment with an alkali or an acid. A negative results from this test does not prove that a substance is not an aldehyde, for many bisulphite addition products are too soluble in water

to appear as precipitates, while others do not combine readily with the reagent. Many ketones, moreover show the same behavior with the reagent as aldehydes.

Compounds of Salicylaldehyde

Salicylaldehyde as a phenol forms salts, ethers, and ethereal salts.

Potassium Salicylaldehyde, C_6H_4 (OK) CHO H_2O, is obtained by adding caustic potash to a solution of the aldehyde in dilute alcohol; it crystallizes in light yellow, nacreous, quadratic tablets, which are readily soluble in water. The compound C_6H_4 (OK) CHO C_6H_4 (OH) CHO is obtained in fine fascicular groups of needles by adding the aldehyde to an alcoholic solution of the potassium salt.

Barium Salicylaldehyde, $(C_6H_4(CHO)O)_2$ Ba $2H_2O$, crystallizes into yellow

needles, which are slightly soluble in cold water.

Copper Salicylaldehyde, $(C_6H_4(CHO)O)_2$ Cu, is a very characteristic salt; when an aqueous solution of copper acetate is added to a dilute alcoholic solution of the aldehyde, the liquid becomes colored emerald green and after a few minutes deposits sparkling crystals, the liquid then presents a most beautiful appearance when placed in sunlight. The crystals become brownish green in drying, and are only slightly soluble in water and alcohol (Ettling)

Lead Salicylaldehyde, C_6H_4 (CHO) OPG.OH, is formed when basic lead acetate is added to an alcoholic solution of the aldehyde; it is a yellow precipitate which dissolves on heating, and separates out on cooling in heavy, light-yellow granules.

Methyl Salicylaldehyde, $C_6H_4(OCH_3)CHO$, is obtained by heating the sodium salt with methyl alcohol and methyl iodide. It is an oily liquid which possesses a faint odor, boils at 238°, and, when perfectly free from salicylic aldehyde, solidifies after some time to tough prisms melting at 35°. It forms a compound with acid ammonium sulphite, which crystallizes in lustrous prisms and is readily soluble in water and alcohol. The potassium sulphite compound also crystallizes well, but it is only soluble in cold alcohol.

Ethyl Salicylaldehyde, $C_6H_4(OC_2H_5)CHO$, was obtained by Perkin in a similar manner to that used for the methyl compound, as a strongly refractive liquid boiling at 247°-249°.

Benzyl Salicylaldehyde, $C_6H_4(OCH_2C_6H_5)CHO$, crystallizes from boiling alcohol

in flat, rhombic prisms, which melt at 46°, and have a faint odor resembling that of cloves. It boils above 360°and forms an imitating vapour.

Acetyl Salicylaldehyde, $C_6H_4(OC_2H_3O)CHO$, is formed when the sodium salt is suspended in ether and treated with acetic anhydride. It is extremely soluble in alcohol, crystallizes in fine, silky needles, melts at 37°, and then solidifies to a mass possessing a satin lustre. Its boiling point lies at about 253°; it combines with the acid sulphites of the alkali metals.

Benzoyl Salicylaldehyde, $C_6H_4(O.CO.C_6H_5)CHO$, is obtained by Perkin by the action of benzoyl chloride on the sodium compound. It is a thick oily liquid, which boils above 360°, and forms the usual compounds with the acid sulphites

of the alkali metals.

Used in preparation of:-

Coumarin, $C_9H_6O_2$, is obtained from salicylaldehyde by heating one part of salicylaldehyde, one part of dehydrated sodium acetate, and one and one half parts acetic anhydride for 8-12 hours on an oil bath at 150°-160°C. using an inverted condenser. The product of the reaction is dissolved in a dilute alkaline solution; the unattacked aldehyde removed by ether. The coumarin is precipitated from its alkaline solution by addition of hydrochloric acid, and is crystallized from benzine.

$$C_6H_4\begin{cases}CHO\\OH\end{cases} + \begin{matrix}CH_3\\CO.OH\end{matrix} = C_6H_4\begin{cases}CH.(OH)\\O - CO\end{cases} + CH_2 \quad H_2O$$

$$C_6H_4\begin{cases}CH\ (OH)\\ O\ -CO\end{cases}CH_2 - H_2O = C_6H_4\begin{cases}CH\\ O.CO\end{cases}CH.$$

Helicin, $4C_6H_4\ (OC_6H_{11}O_5)\ CHO + 3H_2O$, can be synthectically prepared by the action of an alcoholic solution of acetochorohydrose upon salicylaldehyde:

$$C_6H_4\begin{cases}CHO\\ OH\end{cases} + C_6H_7Cl\ (C_2H_3O)_4O_5 + 4C_2H_5.OH$$

$$= C_6H_4\begin{cases}CHO\\ OC_6H_{11}O_5\end{cases} + 4C_2H_5\ OC_2\ H_3\ O + K\ Cl.$$

Ortho Aldehydeophenoxyacetic Acid, $C_6H_4(COH)OCH_2\ CO_2H$, is formed when equal molecules of salicylaldehyde and chloracetic acid are heated together and the fused mass treated with an excess of caustic soda solution of specific gravity 1.2-1.3; the mixture is then heated on the water-bath until it has become almost solid, the acid precipitated by hydro-

chloric acid and re-crystallized from hot water. It forms large, yellow plates, which melt at 132°, and sublime when gradually heated.

Orthohydroxybenzideneacetate, $C_6H_4\langle^{OH}_{CH(OCO.CH_3)_2}$, is formed when salicylaldehyde is heated to 150° with acetic anhydride; it crystallizes from alcohol in thick, hard, transparent tablets, which melt at 103°-104°, and distill with slight decomposition.

The following compounds are obtained in a similar manner.

	Melting P.
$C_6H_4\langle^{OCH_3}_{CH(OCO.CH_3)_2}$, Lustrous prisms---	75°
$C_6H_4\langle^{OC_2H_5}_{CH(OCO.CH_3)_2}$, small prisms-------	88°-89°
$C_6H_4\langle^{OCO.CH_3}_{CH(C.CO.CH_3)_2}$, Needles or pointed tablets----------	100°-101°

Orthohydroxybenzideneoxime, or Salicylic Oxime, C_6H_4 (OH) CH = N.OH, is formed by the action of hydroxylamine on salicylaldehyde, and forms white crystals which dissolve readily in alcohol, ether, benzine, but are insoluble inpetroleum spirit, and melt at 57°.

Hydroxybenzidene - Amedobenzoic Acid, C_6H_4 (OH) CH = NC_6 H_4 CO_2 H, is prepared by mixing warm, dilute aqueous solutions of salicylaldehyde and metamidobenzoic acid. It crystallizes in large, yellow needles, which are very soluble in alcohol and benzine.

Hydrosalicylamide, $N_2(CH.\ C_6H_4.OH)_3$, is formed by the action of ammonia on an alcoholic solution of salicylaldehyde. It forms heavy, light yellow crystals, melting at 300°, and is insoluble in water, slightly in cold, more readily in hot alcohol.

Substitution Products of Salicylaldehyde

Chlorosalicylaldehyde, C_6H_3 Cl (OH) CHO, is formed by the action of Chlorine and salicylaldehyde. It is insoluble in water, and crystallizes from alcohol in rectangular tablets.

Bromosalicylaldehyde, C_6H_3 Br (OH) CHO, is not only formed by the direct action of bromine but also when salicylaldehyde is treated with phosporous pentabromide, the latter compound acting in the same manner as a mixture of bromine and phosporus pentabromide. It crystallizes from ether in small plates, melting at 98°-99°; its alcoholic solution is colored violet by ferric chloride solution.

Methylbromosalicylaldehyde, C_6H_3 Br (OCH_3) CHO, flat prisms, melting point 113°-114°50.

Ethylbromosalicylaldehyde, $C_6H_3Br(OC_2H_5)CHO$, sharp prisms, melting point 67°-68°.

A - Nitrosalicylaldehyde, $C_6H_3(NO_2)(OH)CHO$, is formed together with the B- compound, by boiling salicylaldehyde with dilute nitric acid; the two substances being separated by means of their barium salts. A - Nitrosalicylaldehyde crystallizes in small yellow prisms, which melt at 105°-107°, while its barium salt, $(C_7H_4NO_4)_2 Ba\ 6H_2O$, crystallizes in yellow prisms.

B - Nitrosalicylaldehyde, forms needles, melting at 123°-125°, its barium salt, $(C_7H_4NO_4)_2 Ba\ 6H_2O$, crystallizes in yellow prisms.

Methylnitrosalicylaldehyde, $C_6H_3(NO_2)(OCH_3)CHO$, forms fine, white needles, melting at 88°.

Previous Work

Orthohydroxybenzaldehyde, or Salicylaldehyde, $C_6H_4\begin{cases}OH\ (1)\\CHO\ (2)\end{cases}$

The volatile oil of the flowers of Spiraca Ulmaria was first examined by Pagenstecher, an apothecary of Berne, who discovered in it an acid, the aqueous solution of which is colored violet by ferric chloride, and which was called "speroylwasserstoffsäure," $C_{12}H_6O_6$ (C=6, O = 8) by Sowig, to whom Pagenstecher subsequently found that then the ethereal solution is shaken with caustic potash, this is colored yellow, and on evaporation of the ether an indifferent oil remains behind, which possesses the smell of flowers in a very marked degree, while if the alkaline solution be distilled with phosphoric acid; an acid oil passes over first, followed by

an acid crystallizing in long needles, They now called the former of these spiraca acid, or spiroyl hydride, $C_{13}H_{10}O_4$. About the same time, Piria, working in Dumas' laboratory, found that salicin on oxidation with potassium dichromate and dilute sulphuric acid yields a volatile, oily, aromatic liquid, which he called salicyl hydride, $C_7H_6O_2$. This is isomeric with benzoic acid, and is to be looked up as a hydracid, which, on heating with caustic potash, yields salicylic acid, $C_7H_6O_3$, just as benzoyl hydride under similar circumstances yields benzoic acid. The radicals benzoyl, C_7H_5O, and salicyl, $C_7H_5O_2$, are different oxidation products of the hydrocarbon, C_7H_5. Dumas to whom Pagenstecher showed his prepartions from spiraca, noticed the great similarity of the oil to salicyl hydride and suggested that spiraca

acid was identical with the latter; this had already been proved by Ettling, who named the compound salicylouser spiroylous acid.

The compound was mistaken for and acid because it is at once an aldehyde and a phenol, and therefore forms salts.

Salicylaldehyde was found to occur in the juice of various plants belonging to the genus Spiraca, in the stem and root of Crepis foetida, and in the larvae of Chrysomela popli, which live on willows and poplars, and possess small openings along the body from which salicylaldehyde may be pressed out in oily drops. Ouz also obtained it by distilling the beetle with water.

The aldehyde may also be made from the acid by a reduction process. Salicylic acid is distilled with Methyl alcohol and

sulphuric acid giving gaultheric or oil of bitter almonds. From this we obtain the amide by treating with concentrated ammonia solution. The amide may be reduced to saligenin by means of sodium amalgam, the reaction being carried out at the temperature of melting ice. By the oxidation of saligenin a good yield of salicylaldehyde is obtained. The oxidation is carried out in the following manner.

A mixture of three parts of saligin and three parts of potassium dichromate is treated with 24 parts of water to which 4.5 parts of sulphuric acid diluted with 12 parts of water are added. When the reaction is complete, the mixture is distilled until the distillate passes over clear, and the oil portion then separated from the water. Some of the aldehyde

remains dissolved in the water and is extracted by ether.

If the distillation is continued too long, furfurol passes over, and all preparations made from the aldehyde then become intensely red colored on standing.

EXPERIMENTAL WORK

THEORY

As in most organic preparations we find that there are many ways of producing salicylaldehyde. It is merely a question of finding a process which will give a good yield at a reasonably low cost. According to Friedlander this is realized in converting O-Cresol into the aldehyde. Starting with this body it is but a matter of replacing two hydrogens on the Methyl group with one oxygen, and we have salicylaldehyde. However, the operation is not a simple one to perform. It is evident that is is impossible to replace the hydrogens directly by oxygen. It is possible to replace the hydrogens by chlorine and then by saponification to obtain the aldehyde.

If a phenol is treated with an aqueous solution of chlorine, a trichlorphenol is

obtained. If the phenol is treated with a phosphorus halide and the ester obtained, the chemistry of the ester is very different from that of the phenol. We find that on treating the ester with chlorine gas, in the sunlight, the action is on the side chain only. Therefore if we treat o-cresol with phosphorus-oxy-chloride, we get o-cresolphospaat. $PO(OC_6H_4CH_3)_3$. When this is chlorinated at 160-180°C. the hydrogens of the Methyl group are replaced, one at a time by chlorine. If the chlorination is stopped after two of the hydrogens have been replaced, which may be told by the gain in weight, we obtain o-oxy-benzylideenchlorid phosphoric acid ester, $PO(OC_6H_4CHCl_2)_3$. This on saponification with sodium hydroxide under pressure gives the aldehyde, which is distilled in steam.

This method was carried out in the laboratory using both phosphorus-oxy-chloride and phosphorus trichloride as described in detail later.

EXPERIMENTAL WORK

ACTUAL WORK

An easy laboratory method for the preparation of salicylaldehyde is by the Riemer - Tiemann reaction. In this process, 50 grams of phenol, 100 grams of caustic soda and 160 grams of water are mixed together in a round bottom flask attached to an upright condenser and heated to 50-60°C. Chloroform is then added gradually through the top of the condenser and after each addition the flask is well shaken. A gentle reaction sets in and the temperature rises and at the same time the surface of the brownish yellow solution takes a violet tint, which rapidly fades, the liquid finally assuming a deep red color. When about 75 grams of chloroform has been added, the contents of the flask are boiled for half an hour.

A yellow semi-solid mass separates out of the solution. The unattacked chloroform is now distilled off on the waterbath, the liquid diluted with water and strongly acidified with dilute sulphuric acid. A thick red oil separates out on the surface and is subjected to distillation in steam. An oil, having a faintly yellow color, distills over with the water, and settles to the bottom of the receiver. When drops of oil cease to condense the distillation is stopped. The distillate which contains salicylaldehyde and phenol, is extracted with ether, and the ethereal solution well shaken with a saturated solution of sodium bisulphite. The bisulphite compound of salicylaldehyde separates out in colorless needles, which are filtered, washed free from traces of phenol with alcohol and then decomposed by heating with dilute sulphuric

acid. The aldehyde which separates is taken up with ether, dehydrated over calcum chloride, the ether driven off and the aldehyde distilled. The yield in this case is very low, as only seventeen per cent of the phenol is converted into the aldehyde. This process is not commercially feasible because of the great amount of mechanical manipulation and because at least only seventeen percent of the phenol is convertable into the aldehyde. The yield obtained by this method, as obtained by us, was but four grams.

The reaction undoubtedly takes place as follows:

$$C_6H_5.OH + CHCl_3 = C_6H_4 \begin{matrix} OH \\ OHCl_2 \end{matrix} + HCl$$

$$C_6H_4 \begin{matrix} OH \\ CHCl_2 \end{matrix} + 2NaOH = C_6H_4 \begin{matrix} OH \\ CH(OH)_2 \end{matrix} + 2NaCl$$

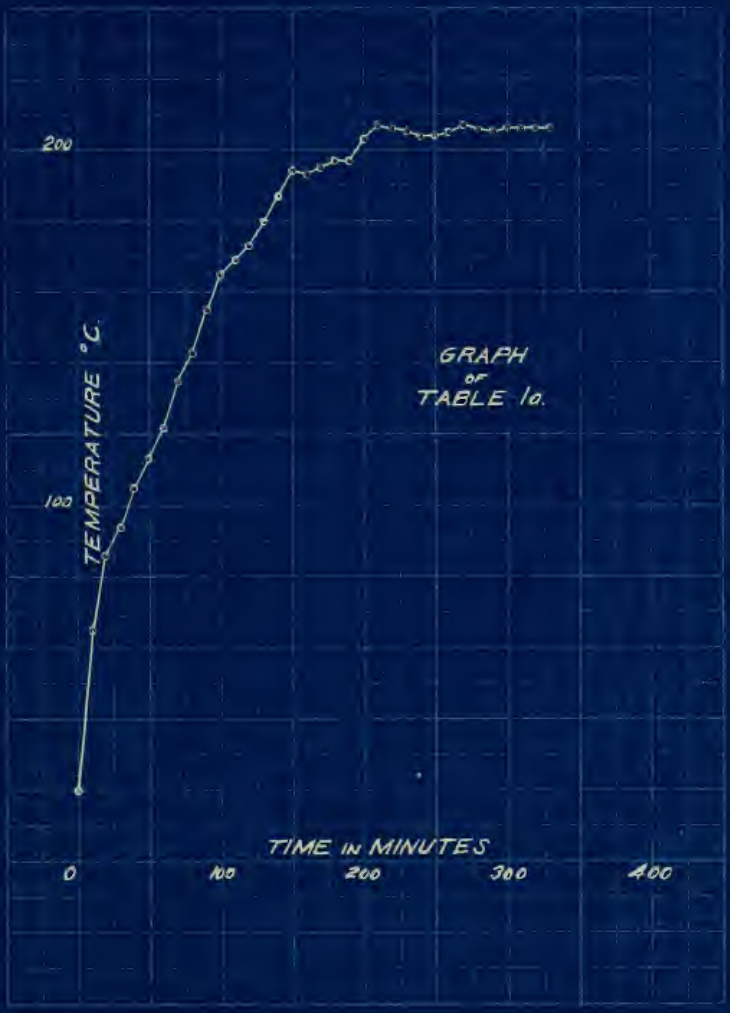
$$C_6H_4 \begin{matrix} OH \\ CH(OH)_2 \end{matrix} = C_6H_4 \begin{matrix} OH \\ CHO \end{matrix} + H_2O$$

The production of salicylaldehyde from o-cresol and phosphorus-oxy-chloride was carried out as follows. To 670 grams of -cresol was added, 280 grams of phosphorus-oxy-chloride. There was slight action with the liberation of heat and hydrochloric acid gas. The mixture was placed in a large flask with an upright or reflux condenser, with the top of the condenser connected to a sodium hydroxide wash bottle to neutralize the acid fumes given off. The flask was then gently heated and started boiling at 65°C. The boiling point gradually rose as the heating was continued until at the end of five hours and thirty minutes it became constant at 206°C. indicating that the reaction has been completed. The color of the liquid changed during the boiling from a dark red to black.

The rise of the boiling point as heat was applied to the mixture of o-cresol and phosphorus-oxy-chloride and the time it required for the two substances to come to a constant boiling point are shown in the following table.

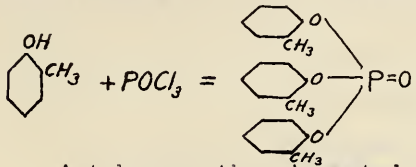
TABLE 1-A.

Time in Minutes	Temperature in °C.
0	20
10	65
20	86
30	94
40	105
50	113
60 (1hr)	122
70	135
80	143
90	155
100	165
110	169
120 (2hrs)	173
130	180
140	187
150	194
160	193
170	195
180 (3hrs)	197
190	197
200	203
210	207


200
100
TEMPERATURE °C.
GRAPH
OF
TABLE 10.
TIME IN MINUTES
0
100
200
300
400

Time in Minutes	Temperature in °C.
220	206
230	205
240 (4hrs)	204
250	204
260	205
270	207
280	206
290	205
300 (5hrs)	206
310	206
320	206
330	206

The reaction of the o-cresol and phosphorus-oxy-chloride probably takes place as shown by the following equation:



A tube was then inserted in the stopper and run to the bottom of the flask so that a stream of chlorine gas could be passed through the liquid. The temperature of the liquid was kept between 160°-180°C. during chlorination. After three and one-

half hours of chlorination white crystals began to form in the condenser tube and continued to form until the tube became congested. The crystals were removed and their melting point determined to be 46° C. They had a faint pleasing odor not unlike that of menthol.

After the chlorination had been carried on for fourteen hours the liquid became so viscous that it was impossible to carry the operation further. It was found that the flask had gained only about one fourth of the required weight.

The following table shows the gain in weight per 30 minutes time for chlorinating and also the temperature control maintained throughout the chlorination.

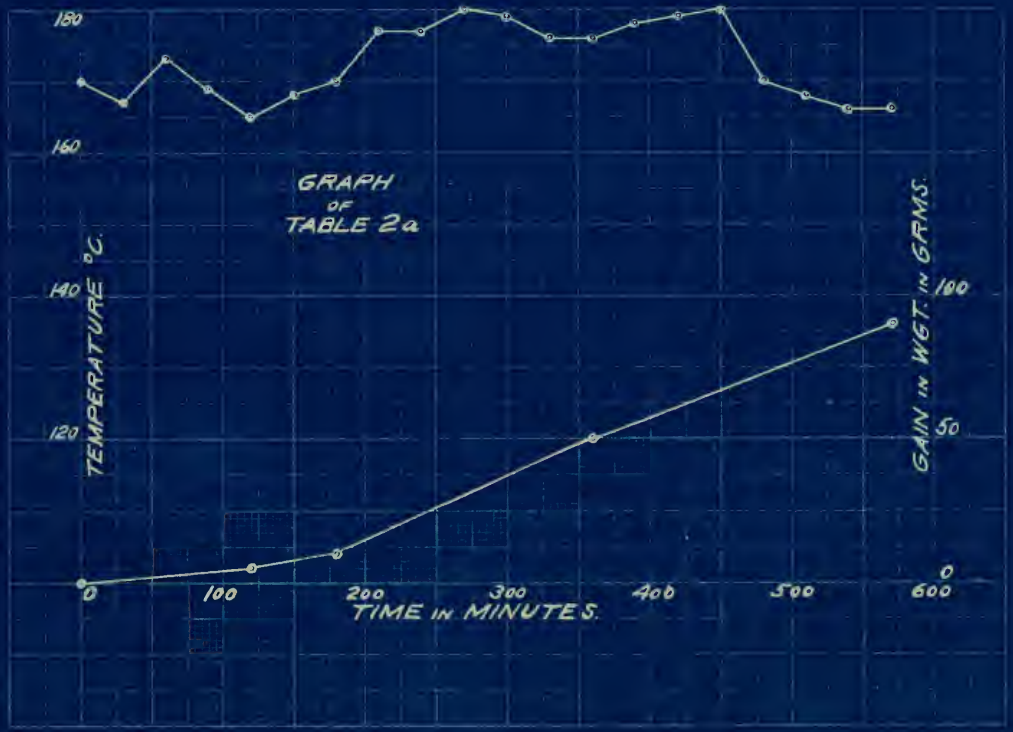
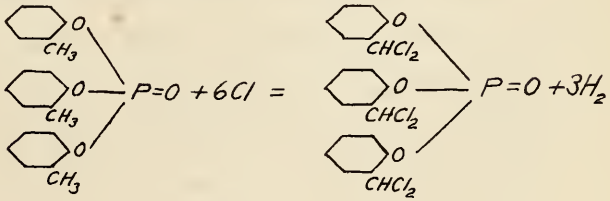

180
160
140
120
TEMPERATURE °C.
GRAPH
OF
TABLE 2a
100
50
0
GAIN IN WGT. IN GRMS.
0
100
200
300
400
500
600
TIME IN MINUTES.

TABLE 2-A

Time in Minutes	Temperature °C.	Gain in weight in grams
0	170	0
30	167	1
60 (1hr)	173	2.5
90	169	3.5
120 (2hrs)	165	5
150	168	7.5
180 (3hrs)	170	10
210	177	17
240 (4hrs)	177	24
270	180	30
300 (5hrs)	179	34
330	176	43
360 (6hrs)	176	50
390	178	56
420 (7hrs)	179	62
450	180	67
480 (8hrs)	170	72
510	168	78
540 (9hrs)	166	85
570	166	90

The equation showing the above reaction probably takes place as follows;

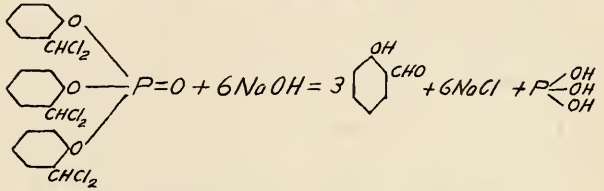


The excess chlorine reactes with the hydrogen given off to form hydrochloric acid gas, which is evolved as one of the products of the reaction.

The liquid upon cooling solidified into a black tarry pitch. A portion of this pitch was saponified with a ten per cent sodium hydroxide solution for a period of ten hours, at the end of which time the contents of the saponification flask was transfered to a distilling flask, diluted with water and strongly acidified with hydrochloric acid, and subjected to distillation in steam. An oil distilled over with the water in the form of an emulsion. When this emulsion ceased to come over the distillation was stopped. The distillate which contains salicylaldehyde is extracted with ether, dehydrated over calcium chloride, the ether driven

off and the aldehyde distilled. The yield was too small to bother with, about 2%.

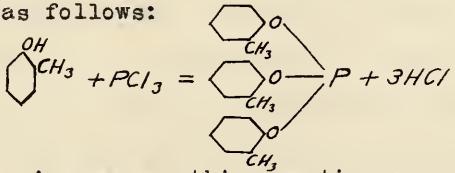
The reaction that takes place during saponification is as follows:



When phosphorus-tri-chloride is used in the preparation of salicylaldehyde from o-cresol instead of phosphorus-oxy-chloride, the same results should be obtained theoretically. The action of the phosphorus-tri-chloride on the o-cresol is much more rapid and goes to completion without the aid of heat as was required with phosphorus-oxy-chloride. The reaction with phosphorus-tri-chloride took only one-half hour to go to completion while the reaction with

phosphorus-oxy-chloride required six hours.

To 150 grams of phosphorus-tri-chloride was added a little at a time from a dropping funnel to 335 grams of o-cresol. The action was rapid and with each addition of phosphorus-tri-chloride the o-cresol boiled vigorously, evolving hydrochloric acid gas. The product formed, o-cresolphorig, $P(OC_6H_4CH_3)_3$ was dark reddish brown in color. The reaction is as follows:



As soon as this reaction was completed, the chlorination with chlorine gas was started. The chlorine reacted at once as was shown by the evolution of heat and a change in color of the liquid.

It became lighter in color and apparently les viscous. As the chlorination proceeded the action became less vigorous and it became necessary to apply heat in order to keep the temperature between 150° and 180°C. After the chlorination had proceeded for two hours the inside of the chlorinating flask became frosted with white needle like crystals much the same as those obtained before. The quantity formed was small and no attempt was made to recover them. About this time the color of the liquid began to change, becoming as a mass a faint bluish green, looking not unlike some grades of lubricating oil. Small portions of it on a glass rod had the appearance of yellow glucose.

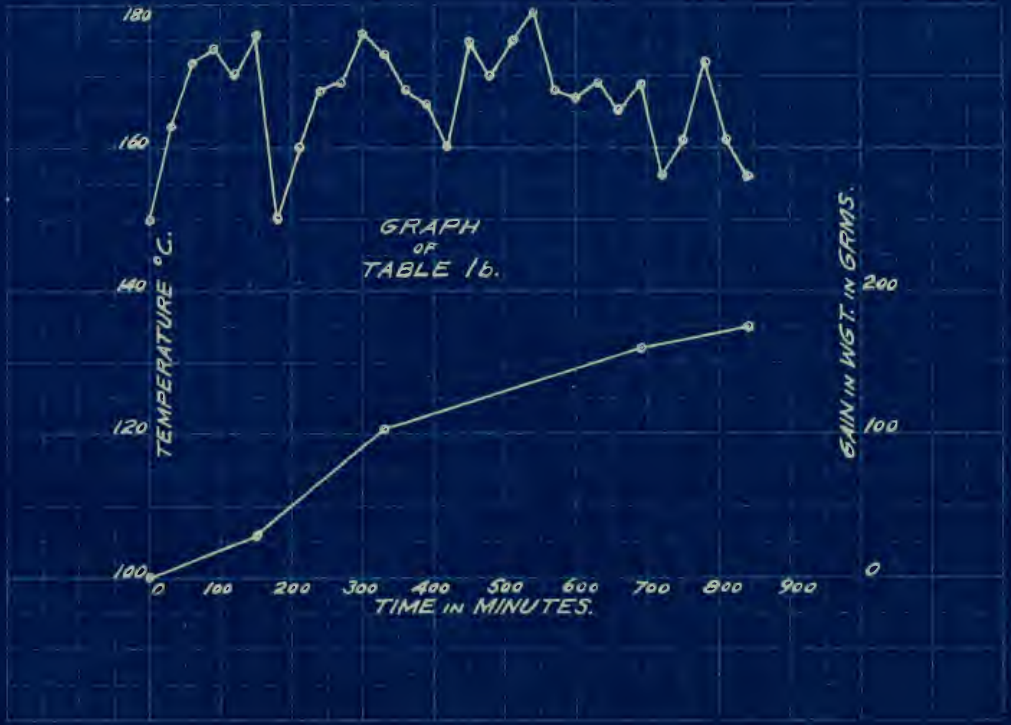
After twelve hours chlorination the liquid had gained 175 grams of the 212

grams it was calculated to gain. As some substance had distilled over inspite of the condenser we had inserted to prevent such action, we considered the reaction complete.

The table below shows the gain in weight per 30 minutes time of chlorinating and also the temperature control maintained throughout the chlorination.

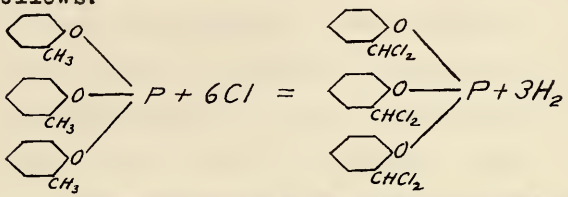
TABLE 1-B

Time in Minutes	Temperature in°C.	Gain in Weight in grams
0	150	0
30	163	5
60 (1hr)	172	12
90	174	18
120 (2hrs)	170	20
150	176	30
180 (3hrs)	150	42
210	160	55
240 (4hrs)	168	66
270	169	78
300 (5hrs)	176	91
330	173	103
360 (6hrs)	168	108
390	166	113
420 (7hrs)	160	117
450	175	122
480 (8hrs)	170	127


GRAPH
OF
TABLE 1b.
TEMPERATURE °C.
180
160
140
120
100
GAIN IN WGT. IN GRMS.
200
100
0
0
100
200
300
400
500
600
700
800
900
TIME IN MINUTES.

TIME	TEMPERATURE	WEIGHT
510	175	132
540 (9hrs)	179	136
570	168	141
600 (10hrs)	167	145
630	169	150
660 (11hrs)	165	155
690	169	160
720 (12hrs)	156	163
750	161	165
780 (13hrs)	172	169
810	161	172
840 (14hrs)	156	175

The reaction taking place here is a very simple one and should take place as follows:

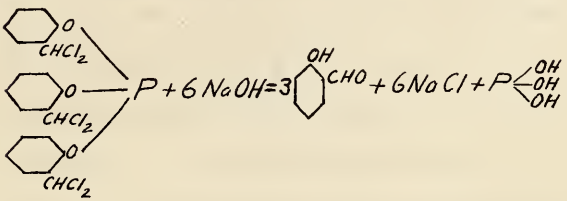


The hydrogen given off will unit with the excess chlorine present to form hydrochloric acid gas. Therefore hydrochloric acid gas will be one of the products instead of hydrogen as it first appears to be given off and complicates matters somewhat as it must be taken care of.

The product of chlorination was then saponified with a ten per cent sodium hydroxide solution for a period of ten hours. 400 c.c. of sodium hydroxide solution was used for 100 grams of the chlorination product. At the end of ten hours the substance took on the appearance of a spongy red mass which gave an intense violet color with ferric chloride proving the presence of the aldehyde. This red mass, containing the aldehyde, was transfered to a distilling flask, diluted with water and strongly acidified with dilute hydrochloric or sulphuric acid, then subjected to distillation in steam. An oil, having a faintly yellow color, distills over with the water, and settles to the bottom of the receiver. When drops of oil cease to condense the distillation is stopped. The distillate

which contains salicylaldehyde is extracted with ether, dehydrated over calcium chloride, the ether driven off and the aldehyde distilled. The aldehyde distilling over between 195° and 198°C. was caught and weighed, the yield calculated and found to be 23.4%.

The reaction taking place during saponification is probably as follows:



SUMMARY

The first process used to obtain the aldehyde employed the Riemer-Tieman reaction. This process yields only a small percentage of salicylaldehyde and is only valuable as a laboratory preparation of the aldehyde.

In the process using o-cresol and phosphorus-oxy-chloride several difficulties were met with. In the first place the chlorination did not appear to go the way it should and resulted in the formation of a black pitch instead of a heavy oil. This pitch upon saponification with a ten percent sodium hydroxide solution for a period of ten hours gave a yield of salicylaldehyde which was too low to make the process of any value.

From the process using o-cresol and phosphorus-tri-chloride the best results

were obtained. The yield varied from fifteen to twenty-three percent depending, we suppose, upon the length of saponification and the strength of the sodium hydroxide solution used. To obtain the correct strength of sodium hydroxide solution to use in the saponification and the time of saponification necessary, required more time than we had to devote, therefore out time of saponification and strength of sodium hydroxide solution may not give the maximum yield. The yield obtained warrants our choosing this process as the most feasible of those tried by us.

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